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7 October 1999

MEMORANDUM FOR PRS (Contractor Pu

FROM: PROI (TI) (STINFO)

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-¹⁹⁹⁹~~99~~-0184,
Ismail Ismail, ERC, and Tom Hawkins, PRSP, "Physical and Chemical characterization of Ultrafine
Aluminum Powders"

ACS Pacific Conference on Chemistry and Spectroscopy, 6-8 Oct 99

(Statement A)

**PHYSICAL AND CHEMICAL CHARACTERIZATION
OF ULTRAFINE ALUMINUM POWDERS**

**I. M. K. Ismail
ERC, Inc., c/o AFRL/PRSP**

and

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Edwards Air Force Base, Ca 93524-7689**

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INTRODUCTION

- Compared to “regular” aluminum powders, ultrafine aluminum UFAl enhances the burning rate of propellants.
- Smaller UFAl particles have a large surface area which enhances the burning rate, they also have a large percentage of Al_2O_3 which reduces the ISP of the propellants.
- Open literature indicates UFAl powders can be prepared by several methods:
 - Electro-explosion of metal wires: Argonide Corporation (www.argonide.com)
 - Plasma torch vaporization & condensation (dollar.eng.sunybs.edu/isl/ctsr/huggets/nugget1/).
 - Catalytic thermal decomposition of AlH_3 adducts (MRS 457, 131, 1997).

BACKGROUND

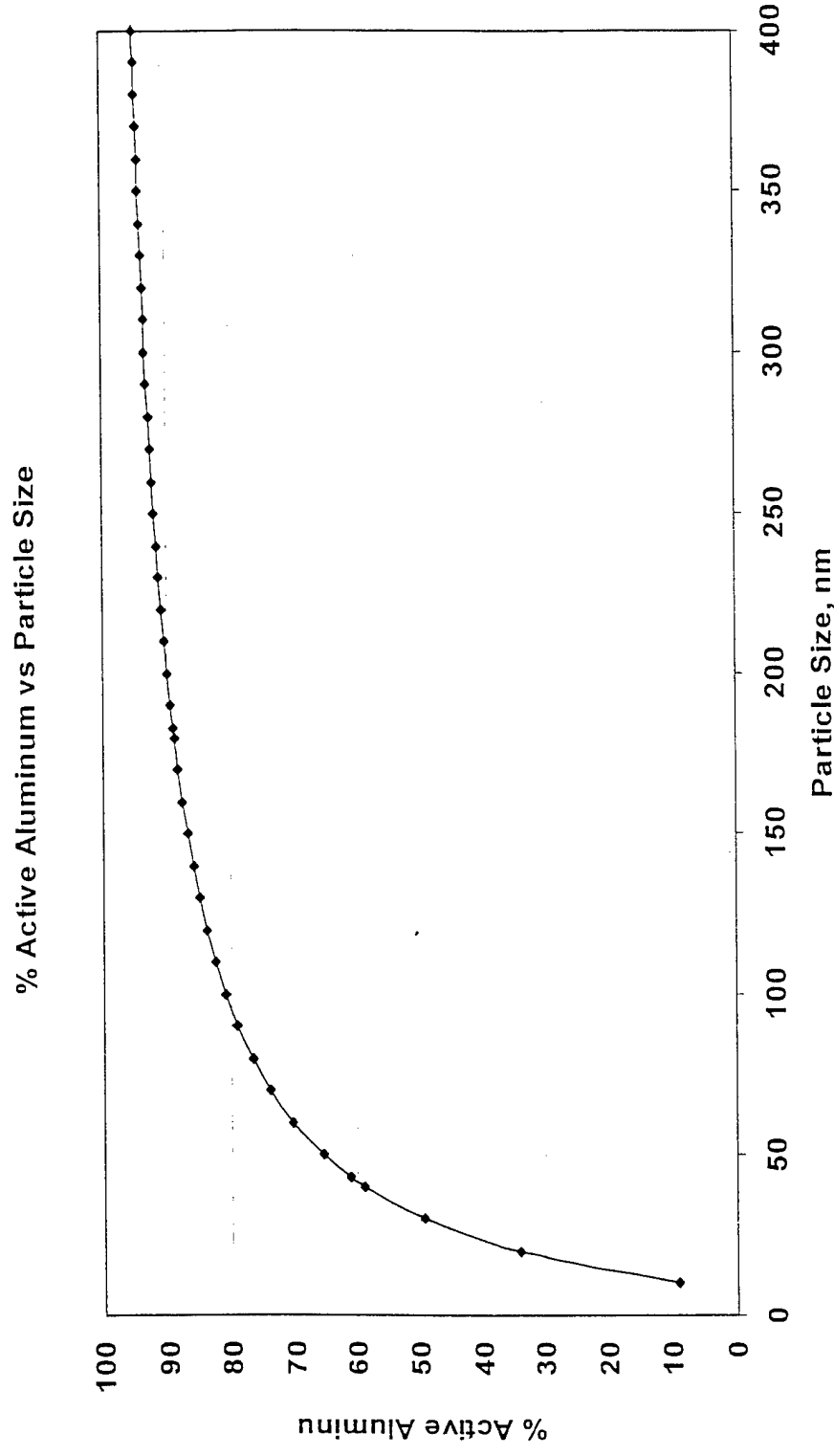
- Metallized gelled propellants such as $O_2/ RP-1/ Al$ and gelled hydrogen $O_2/ H_2/ Al$ have been considered by NASA - nanoparticulate gellants by NASA/TRW (www.grc.nasa.gov/WWW/TU/launch/China)
- With UFAl powders, there is a potential for reduced gellant masses and agglomeration on nozzle.
- Higher rocket performance is needed for future missions.
- Different sources (DOD, NASA and private sector) have confirmed that the addition of UFAl powder to propellants increases burning rate by as much as a factor of 3.
- Open literature sites many methods of preparations but less emphasis has been given to properties of ultrafine particles.
- Due to their low bulk density, the powders are difficult to handle and their characterization is a challenge.

OBJECTIVES

- Develop techniques and methodologies for physical and chemical characterization of UFAl powders.
- Characterize the powders obtained from different sources.
- Develop a methodology to study the kinetics of reactions between UFAl and oxygen (oxidation) or nitrogen (nitridation) at different conditions.
- Estimate diffusion parameters and limitations for the reactions.
- Determine composition and crystallographic structure of solid residues left after the oxidation and nitridation reactions.
- Generate simple computer models to address the thickness of pre-existing Al_2O_3 layer on the particles of UFAl powders.

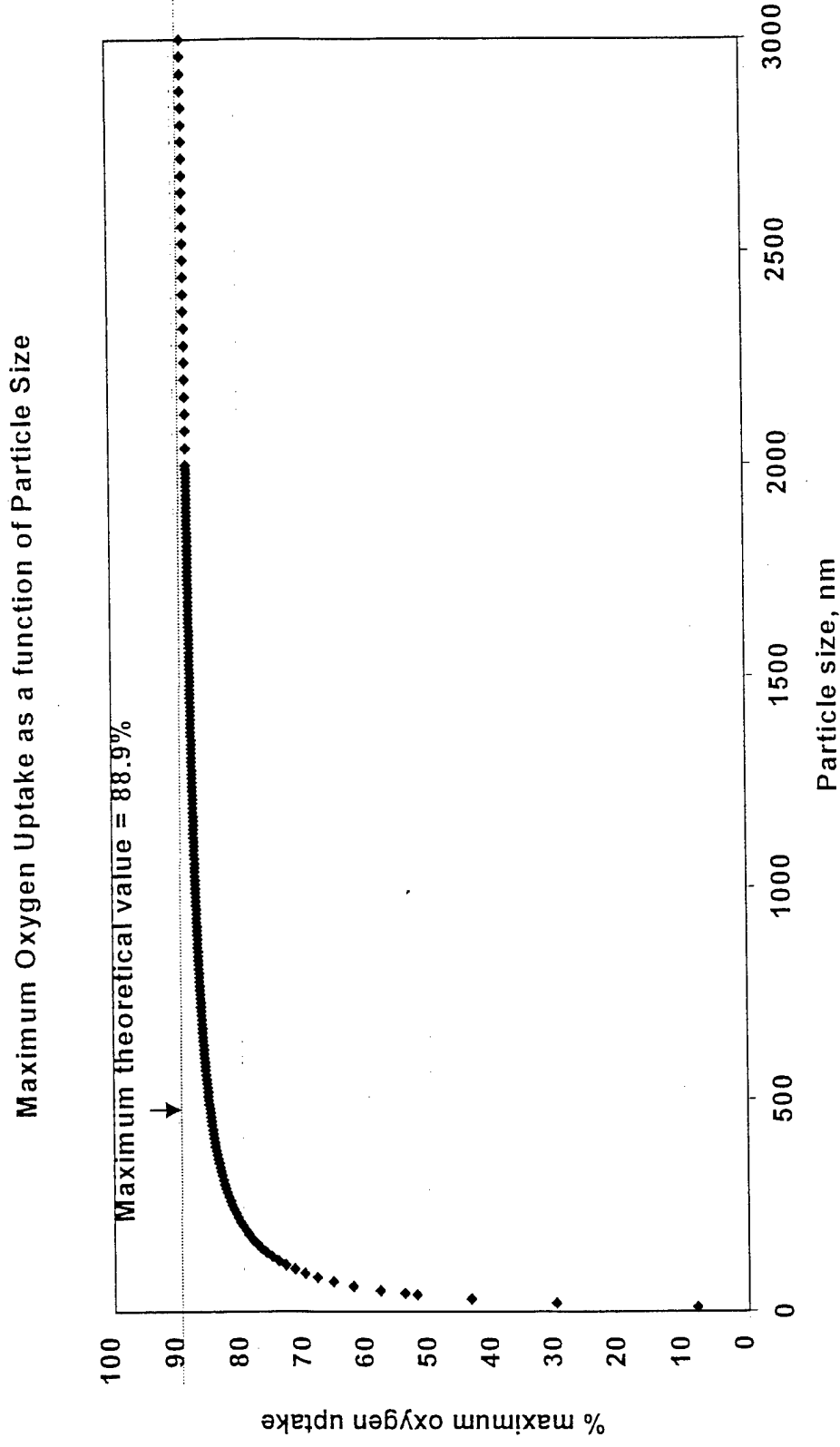
**As particle size decreases, the percent of active aluminum decreases.
Performance (ISP) of aluminized propellant may be lowered.**

(Pre-existing oxide thickness is arbitrarily taken here as 2.5 nm)



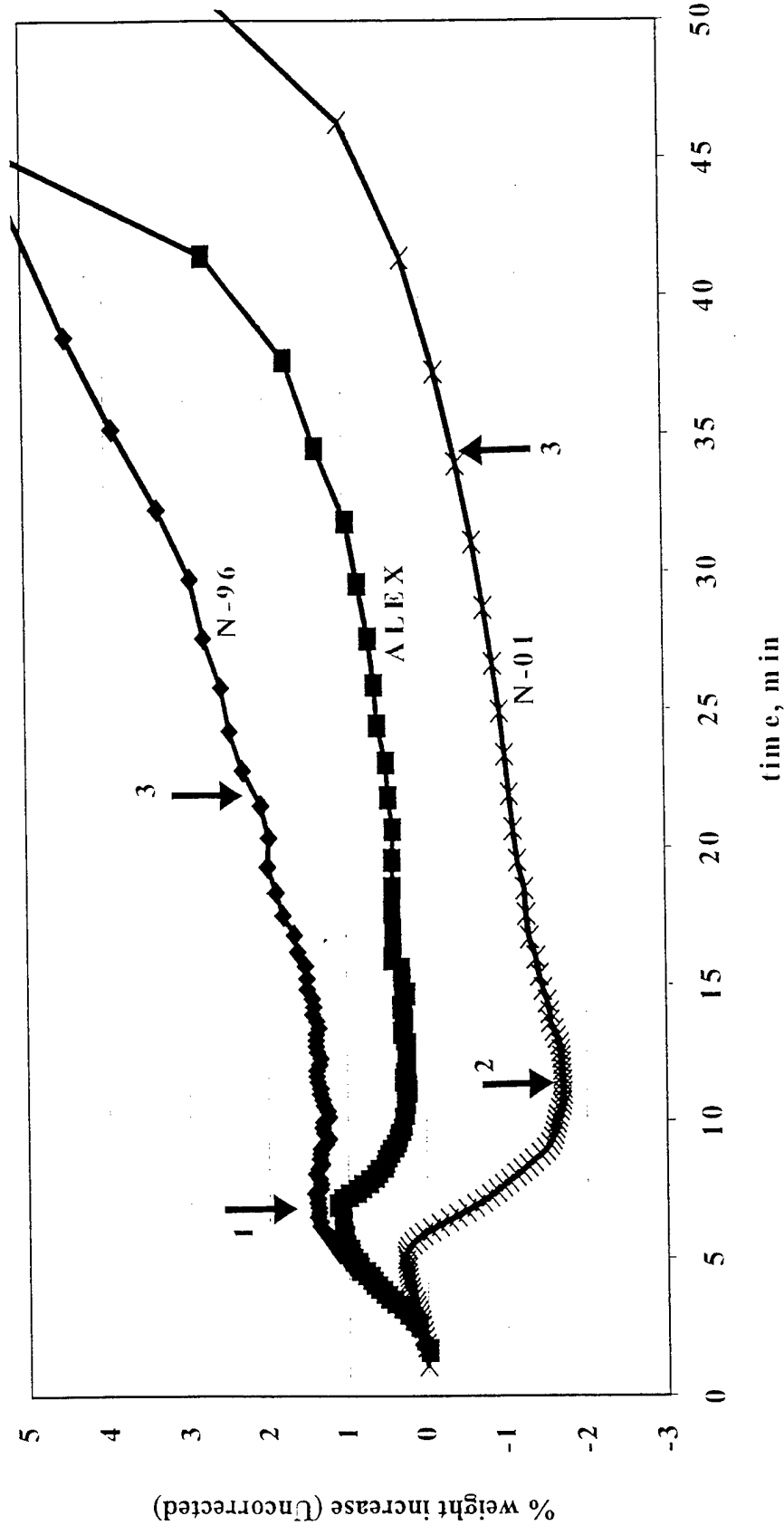
- **Recommend to develop a technique for thin coating the particles immediately after they are born.**

Theoretical oxidation of Al particles of different sizes with a constant starting (pre-existing) Al_2O_3 layer thickness = 2.5 nm



Based on the 2.5 nm assumption, UFAl particles have less active aluminum and requires less oxygen than the state-of-the-art aluminum particles.

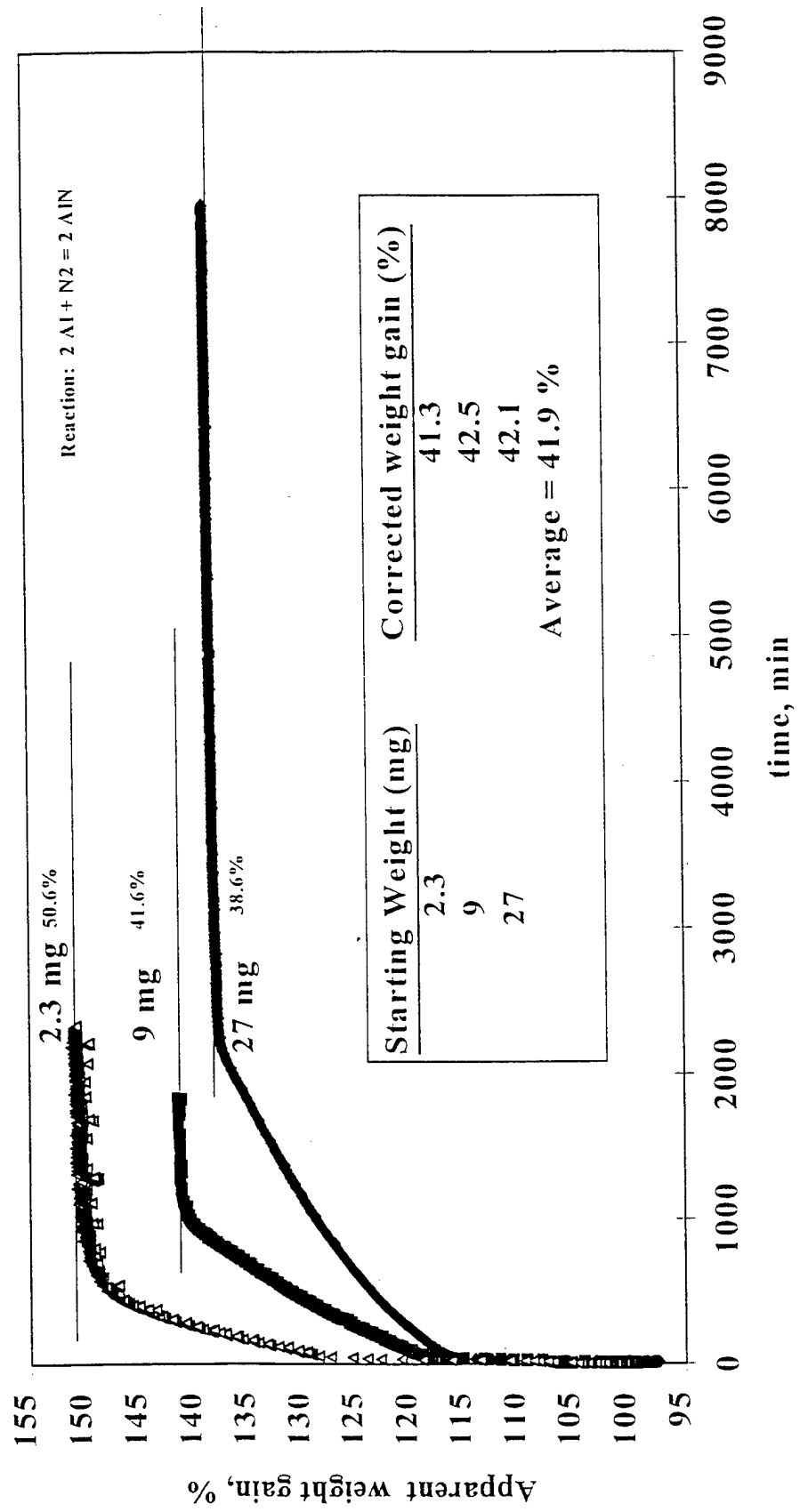
The nitridation reaction of UFAl powder at the early stages of heat-up includes three main steps: 1. Weight gain due to change in gas density (buoyancy effect). 2. Weight loss due to release of moisture and volatiles (buoyancy effect). 3. Weight gain due to oxidation (or nitridation) plus buoyancy effects.



- Corrected weight gain = apparent weight gain + maximum weight loss - buoyancy effects

Apparent weight gain is a function of sample size: diffusion through UFAl bed is significant – smaller samples show excess weight gain

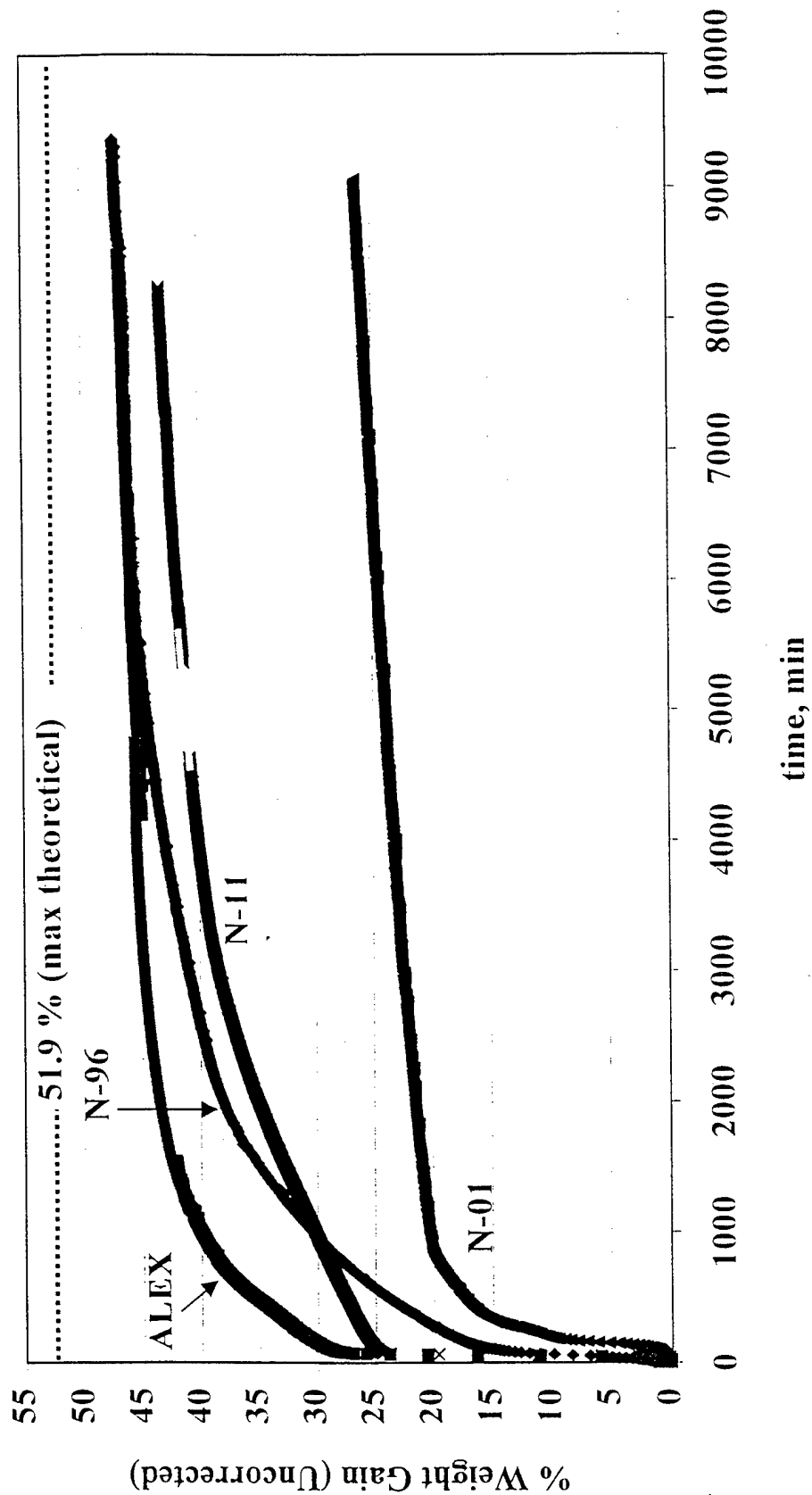
Effect of Al bed height at 600 C on kinetics (Indian Head UFAl powder)



- The average corrected weight gain is independent of sample size
- Error = $\pm 0.6\%$

Nitridation reaction of UFAL

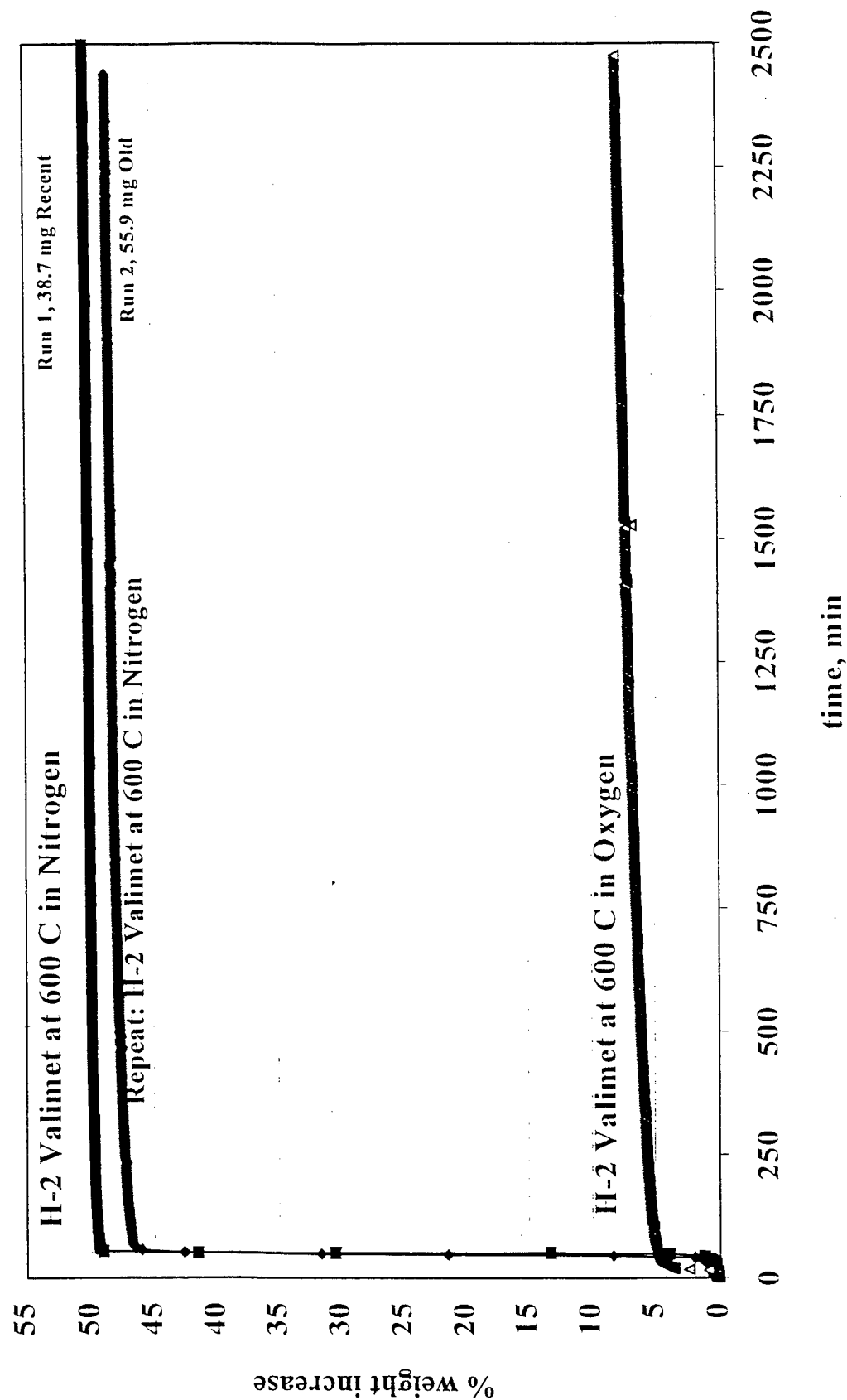
Reaction between UFAL and N₂ (50 cc/min) at 600 C



Nitridation and oxidation reactions of H-2 Valimet at 600 C.

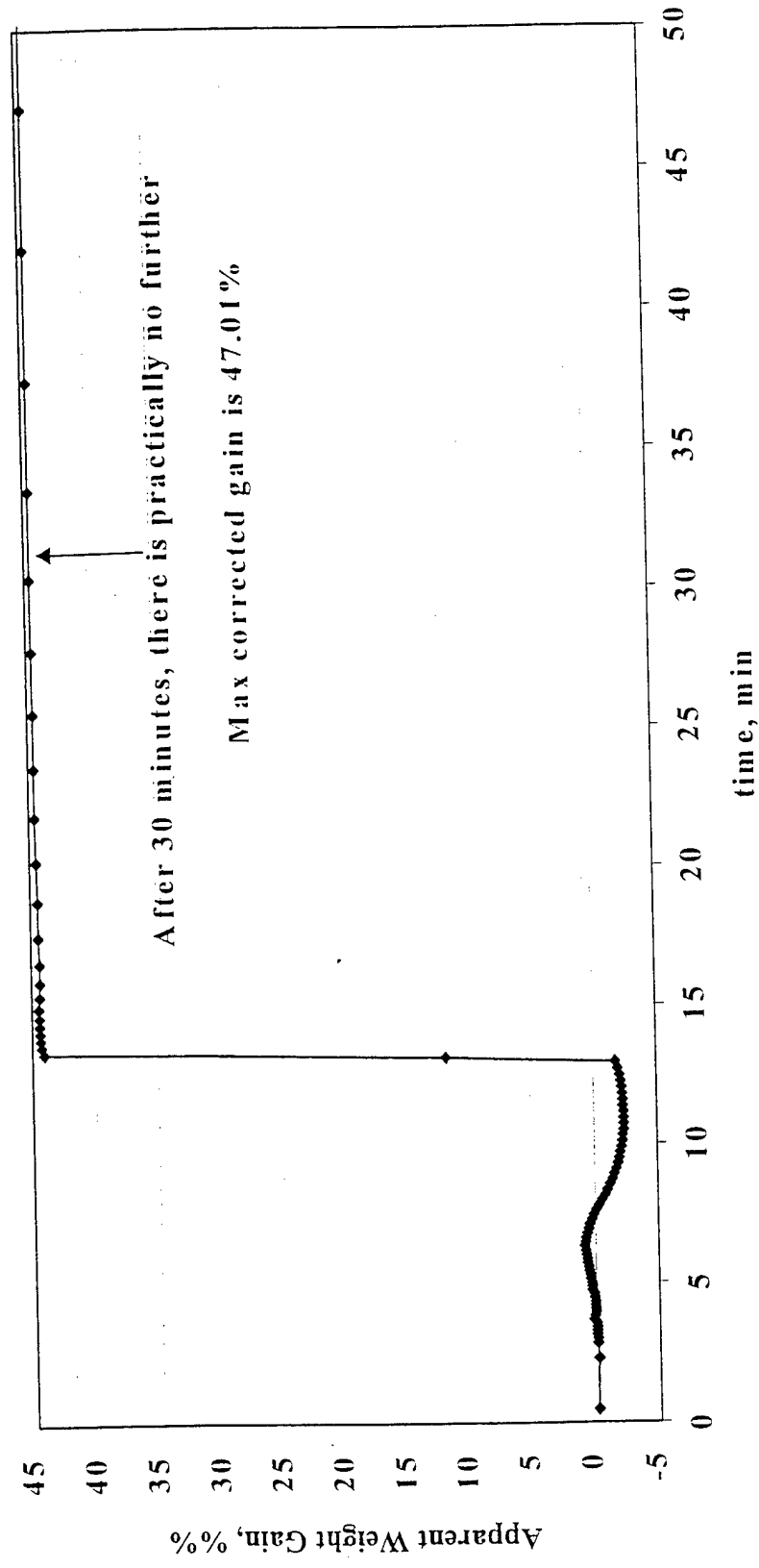
In nitrogen, the reaction is completed in ~ 1 hour.

In oxygen, less than 10% of active aluminum was oxidized.



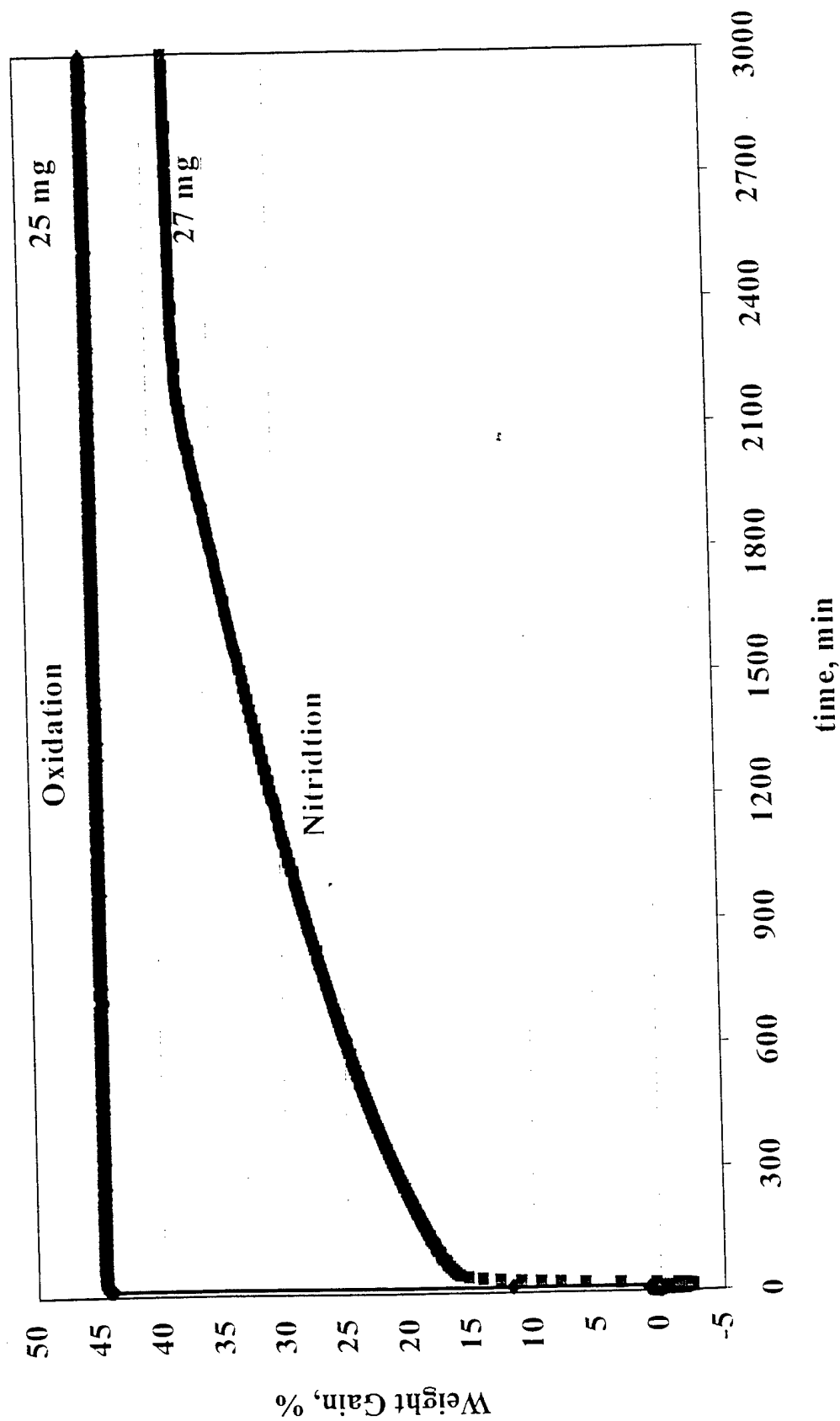
Oxidation of UFAl (43 nm diameter) in oxygen at 600 C

Indian Head UFAl (43 nm diameter) at 600 C in Oxygen (not air) - new bucket - 25 mg



- The oxidation is completed in 15 minutes

Nitridation and oxidation reactions of UFAL-IH (43 nm) at 600 C.
In oxygen, the reaction is fast and reaches a constant value in ~30 minutes.
In nitrogen, the reaction is considerably slower.



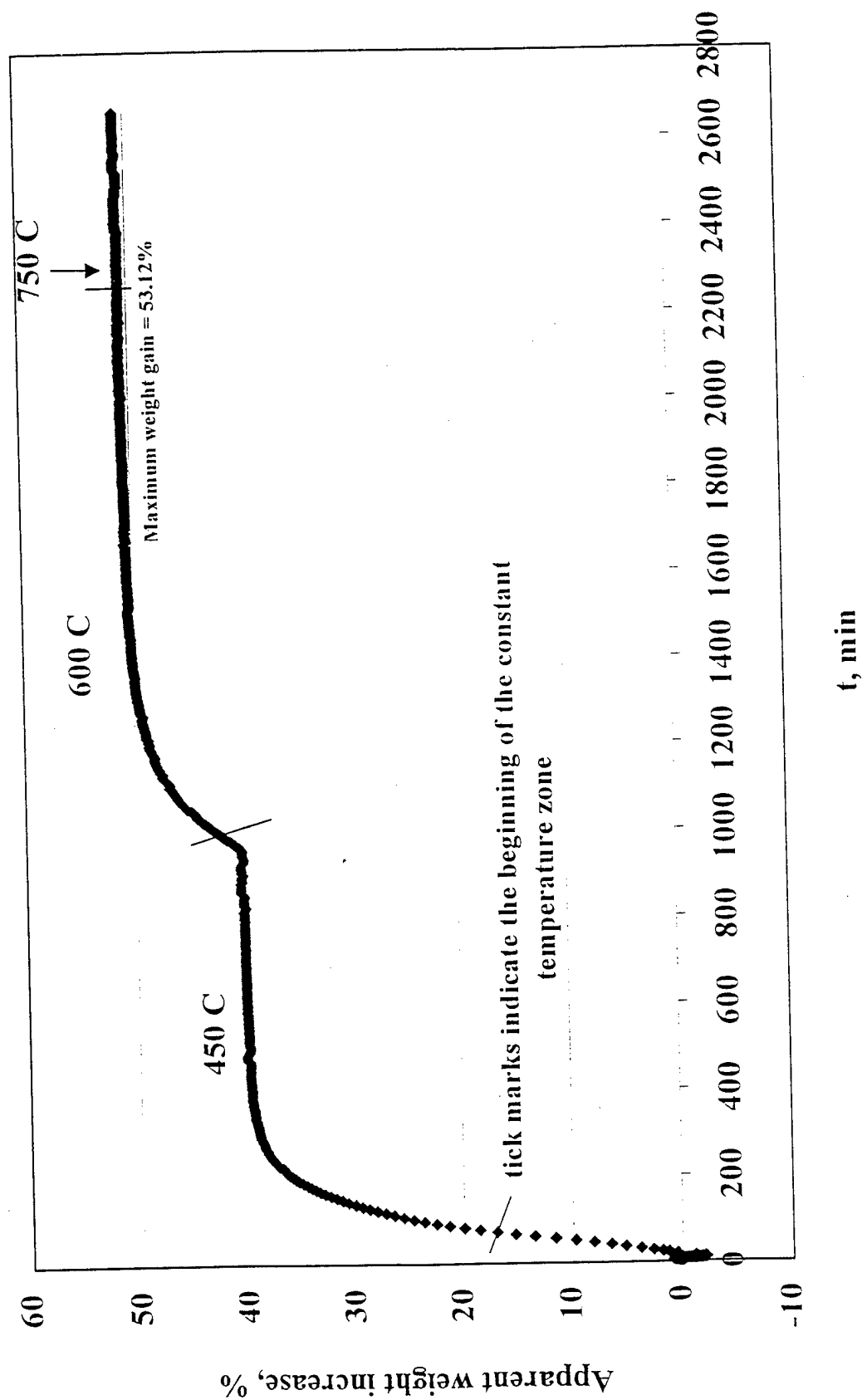
Dr. Hawkins favorite page !!

- The current work indicates that there exist different types of diffusion limitations on the oxidation and nitridation reactions. The rate determining step differs with each gas.
- Under similar reaction conditions, the rate determining step is strongly controlled by the starting particle size of Al powder.
- The diffusion of N_2 through AlN at 600 C does not impose limitations on the kinetics of the reactions. The nitridation of the largest particle size was completed in an hour.
- However, the diffusion of oxygen through Al_2O_3 does impose limitations which can be reduced by raising sample temperature. Smaller particles oxidize faster than larger particles (a result of the length of diffusion distance).
- Diffusion limitations of nitrogen through the aluminum bed can play an important role in nitridation kinetics. Such limitations are either due to a high (physical packing) density of the finer particles which limits the flow of species to active aluminum surface, or a high probability of forming agglomerates as a result of melting.

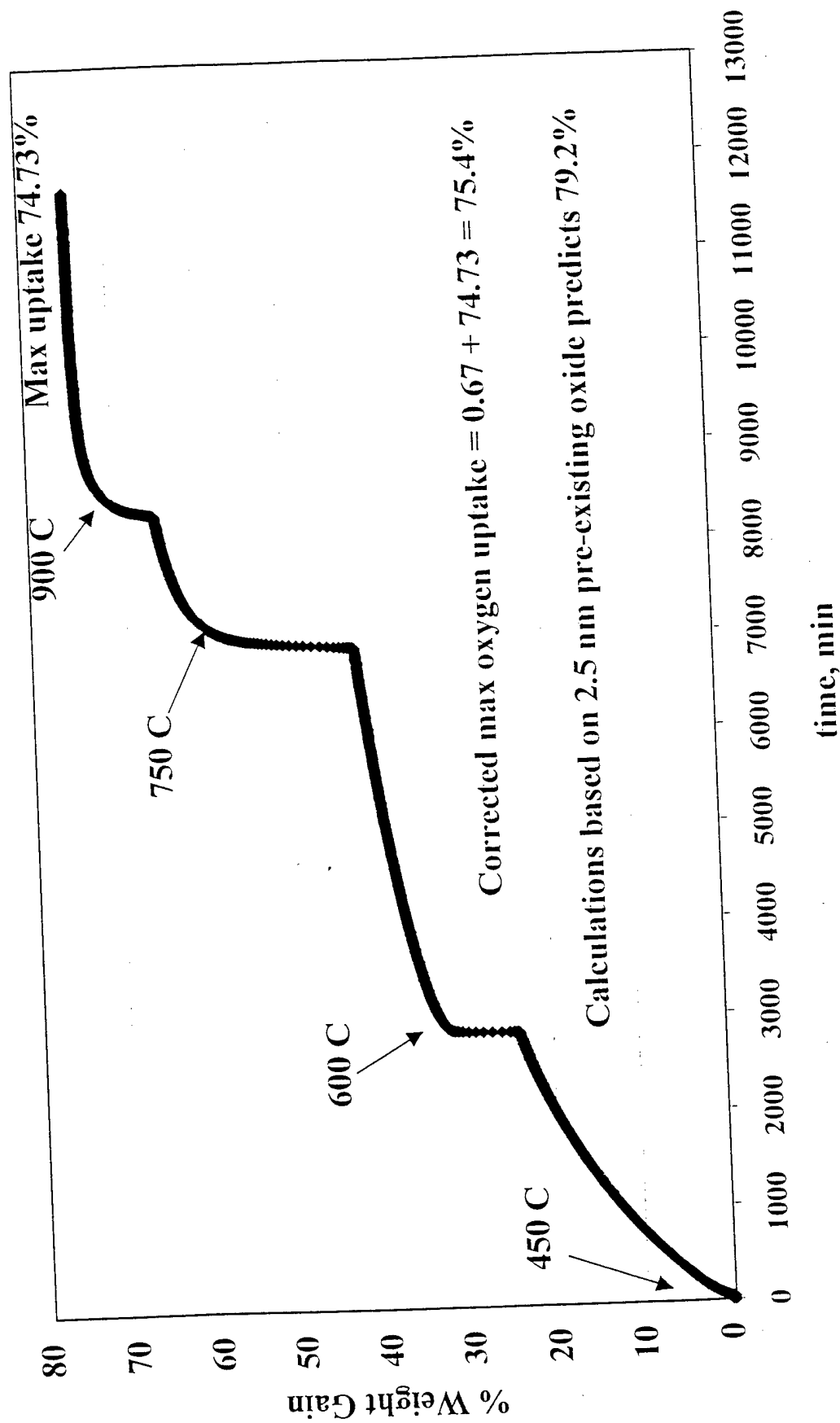
THE VOLUME OCCUPIED BY
PARTICLES IS INDEPENDENT
OF PARTICLE SIZE FOR
MECHANICAL ENGINEERS
WHAT DOES THIS MEAN IN
REALLY?

Tom
C. F. H.

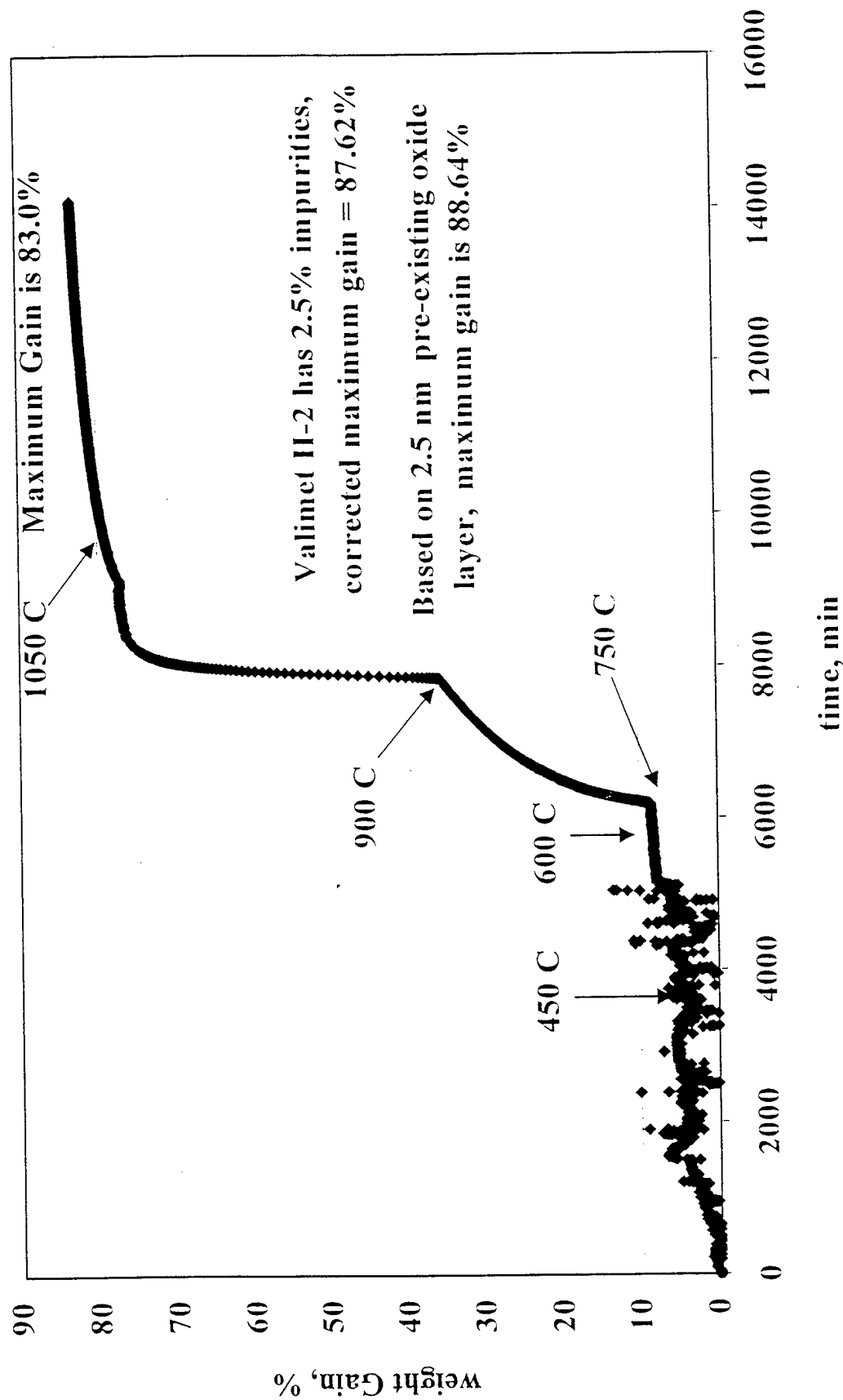
Step oxidation of UFAl-IH (46 nm) at different temperatures. With this particle size, the reaction is almost completed at 600 C.



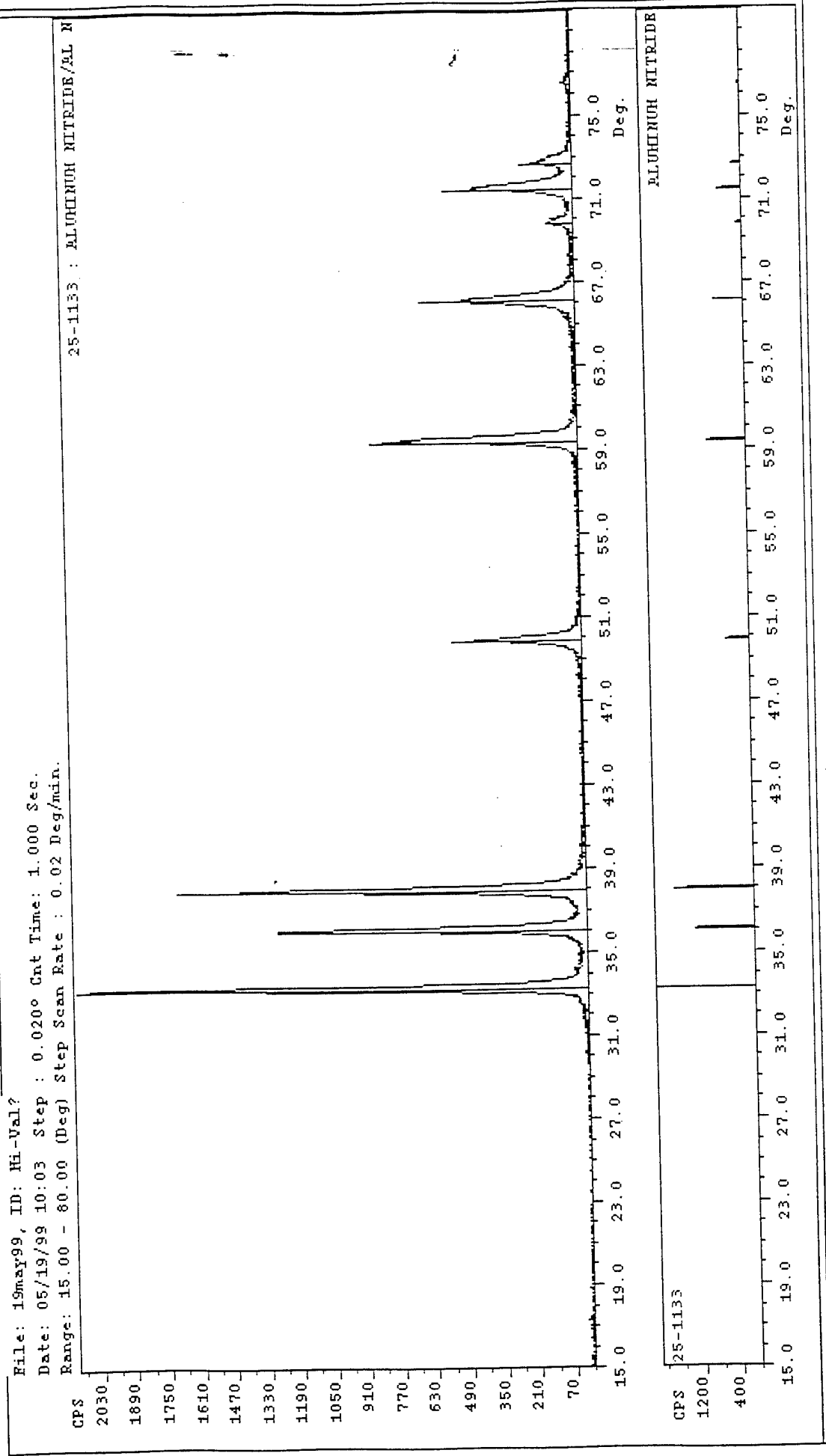
Russian ALEX (183 nm) in O₂ at 450, 600, 750 and 900 C: The reaction is almost completed ONLY at 900 C.



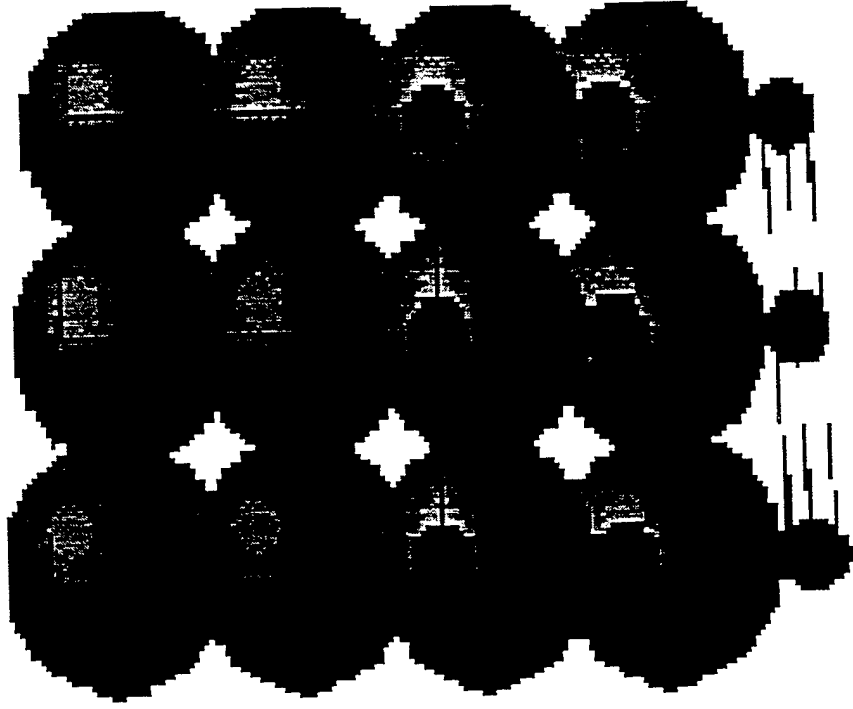
Valimet H-2 (1035 nm) in oxygen at 450, 600, 750, 900, 1050 C. The reaction is completed at 1050 C. Oxidation at 450 and 600 C is slow.



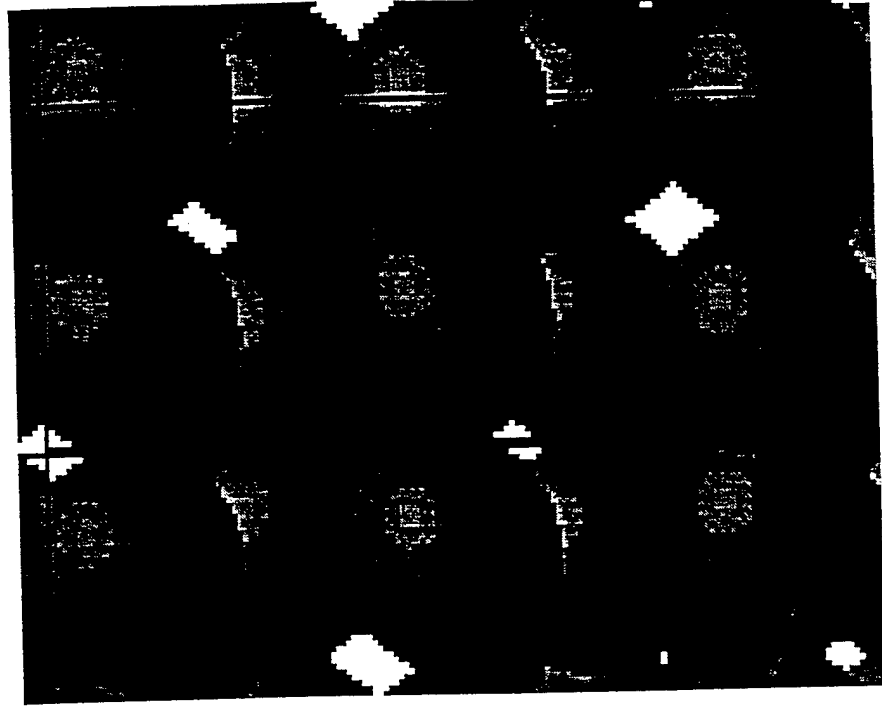
X-ray diffraction data on residue left after nitridation of Valimet H-2.
Major component: 95% + hexagonal aluminum nitride.
Minor: cubic aluminum nitride and cubic aluminum oxy-nitride.



Crystal structure of AlN and Al_2O_3 : the nitride has more interstitial space than the oxide.



AlN



Al_2O_3

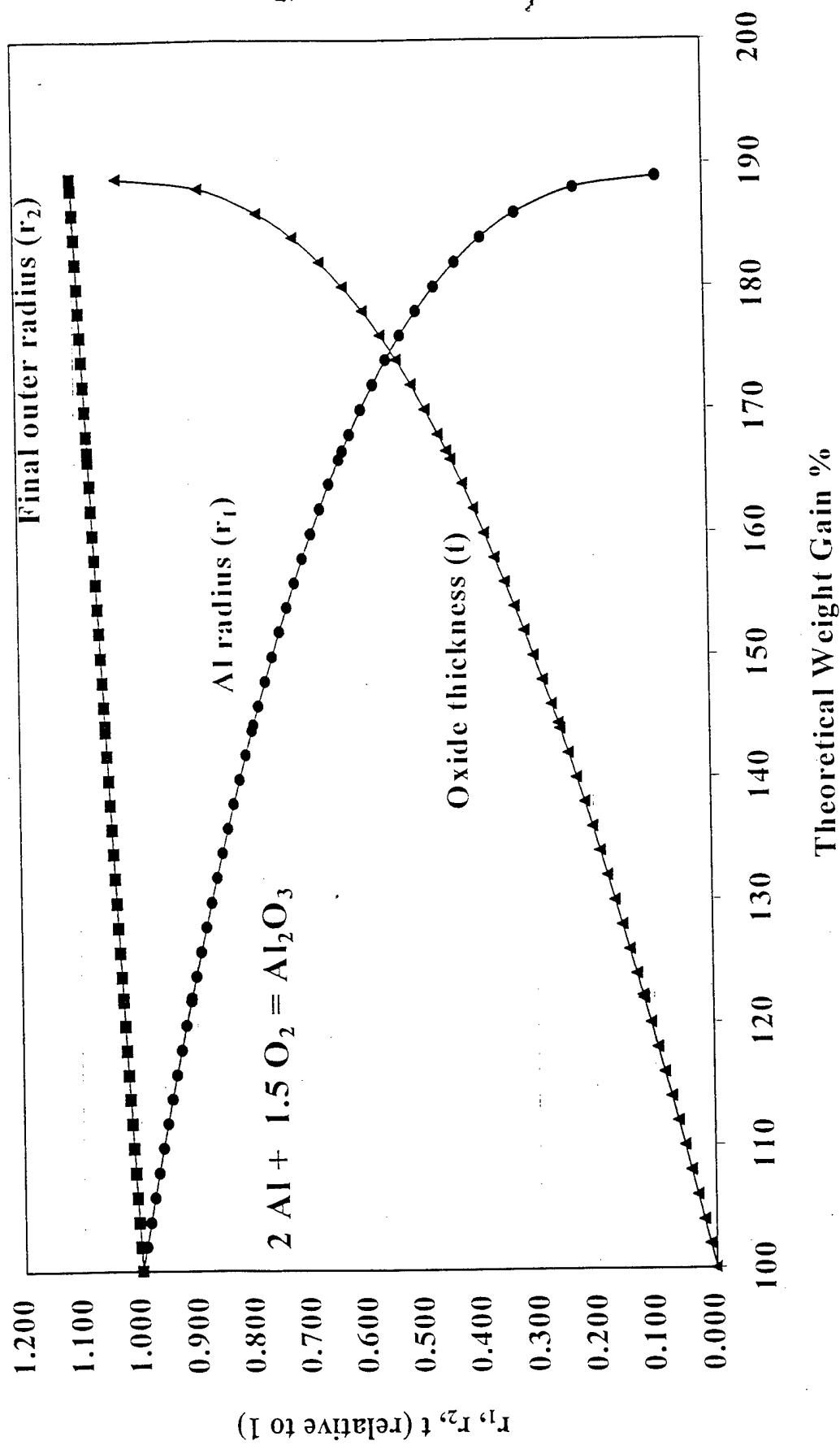
- The structures suggest that diffusion of gases through the oxide crystal is more restricted than through the nitride crystal.

Theoretical considerations and computations

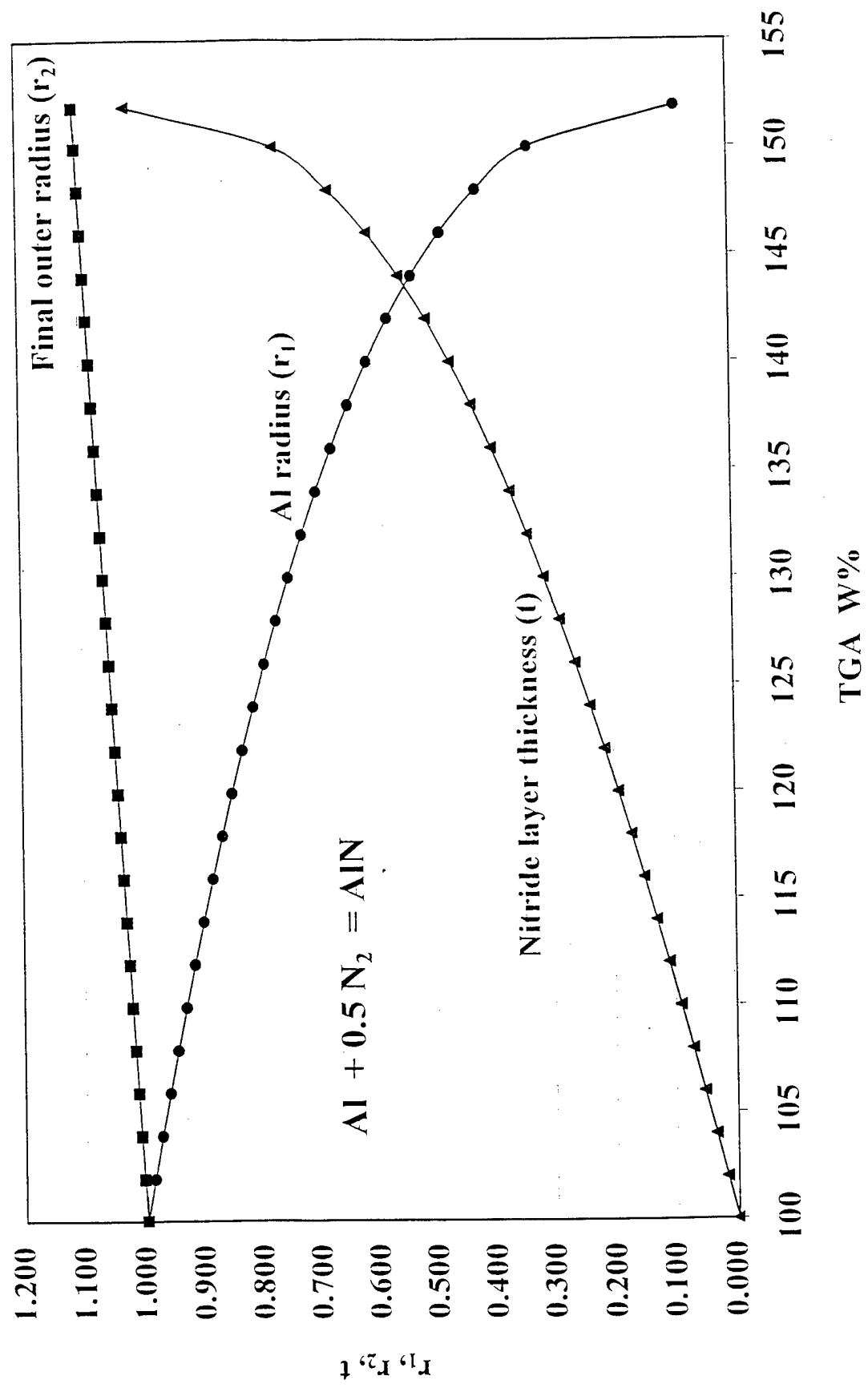
- When aluminum reacts with nitrogen or oxygen, the particles swell.
- All particles of different sizes have a pre-existing external Al_2O_3 layer covering a core of active aluminum.
- The thickness of the oxide layer is assumed constant for all particles. It is taken here as 2.5 nm.
- As the process propagates, the radius of aluminum core, r_1 , decreases.
- At a given time interval, the radius of the entire particle (aluminum core + aluminum nitride layer + pre-existing Al_2O_3) is taken as r_2 .
Thus: $r_2 - r_1 - 2.5 \text{ nm} = \text{thickness, } t, \text{ of AlN (or } \text{Al}_2\text{O}_3) \text{ formed during reaction.}$

- Densities of Al, AlN and Al_2O_3 were taken as 2.70, 3.26 and 3.84 g/cc.

Oxidation of Aluminum (starting particle size = 1.00 nm)



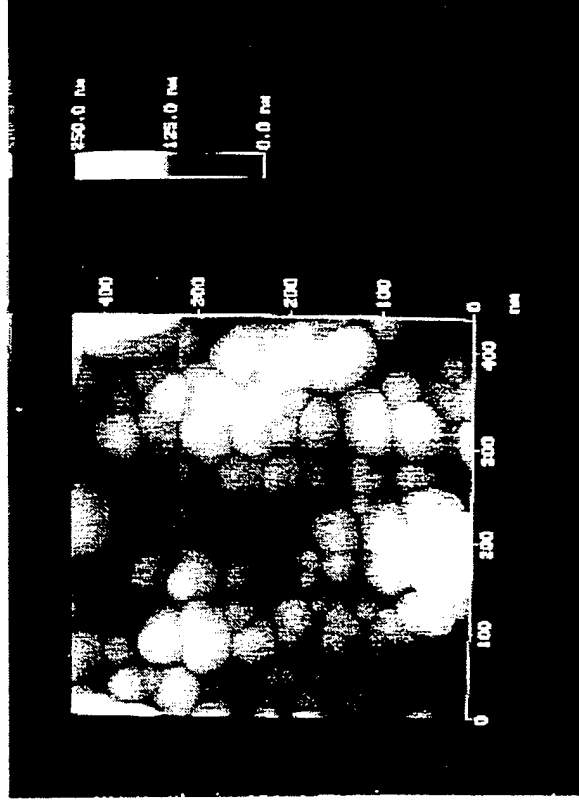
Nitridation of Aluminum (starting particle size = 1.00 nm)



STM Photos of UFAl-IH Powders

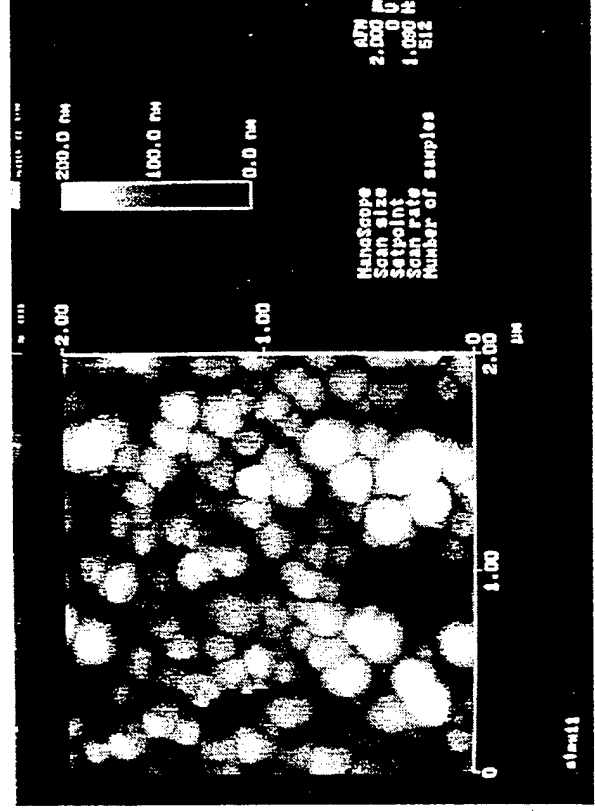
IH

Average size: 43 -64 nm

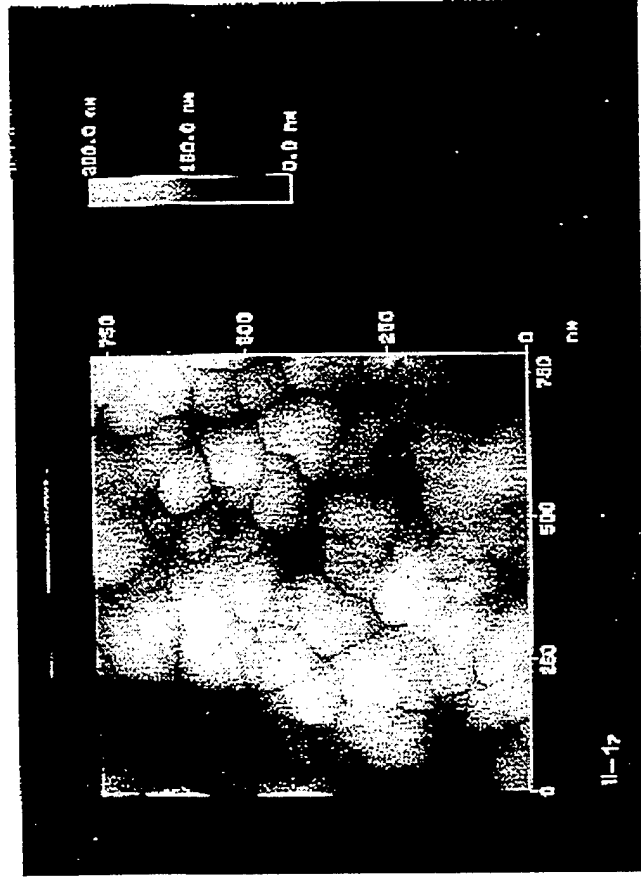


ALEX

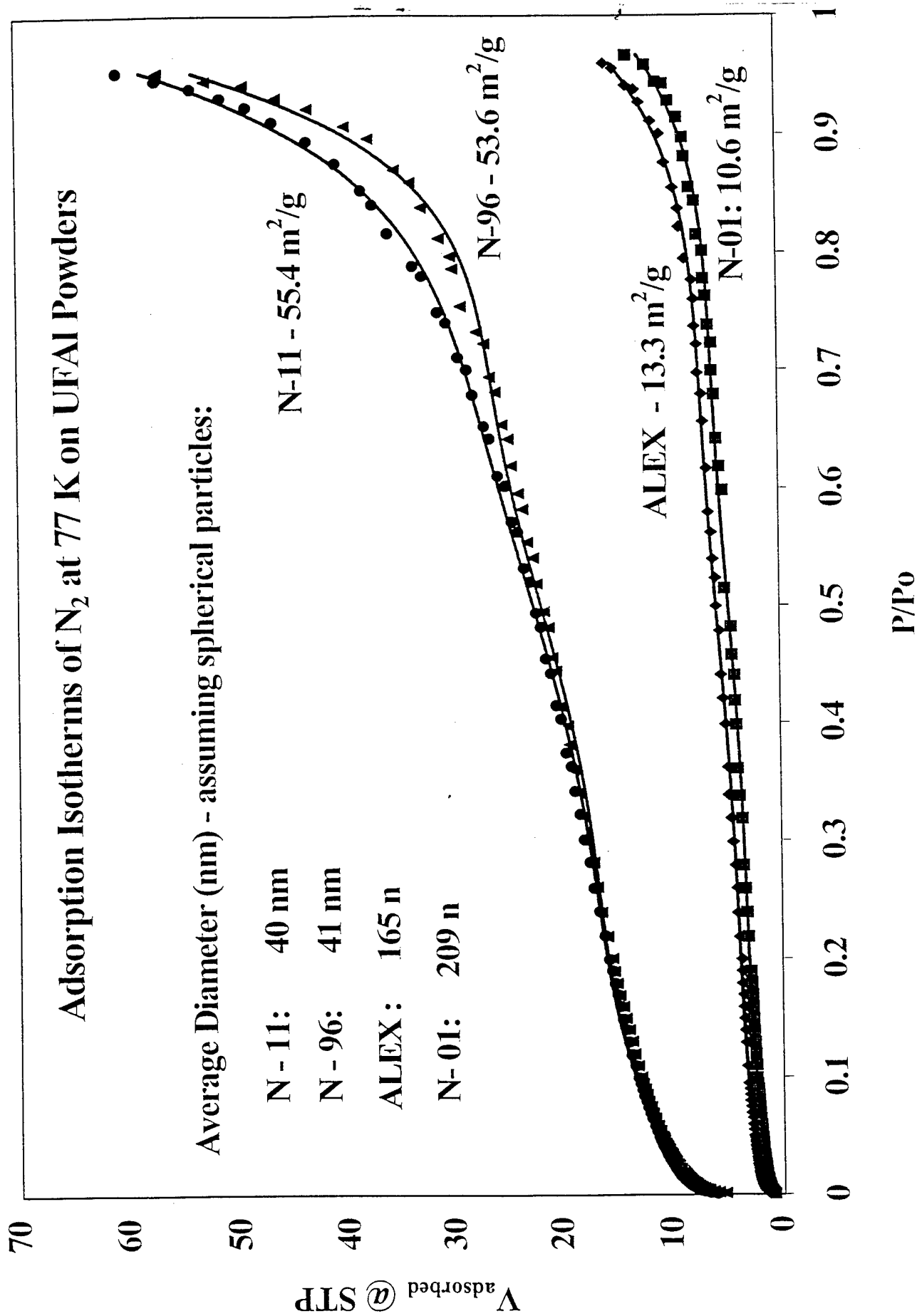
Average size: 160-190 nm



SEM and STM of AlN after complete nitridation of UFAL-III powder.



The ultrafine particles agglomerates moderately during the nitridation reaction at 600 C. Individual particles are still seen.



Surface Area and Estimated Average Particle Size for Ultrafine Aluminum Powders

Sample ID	Average A_s m^2/g	BET Average Particle size (nm)	Average Particle size from STM
ALEX	13.3	165	177
RF-A	48.1	46	40-120 nm (agglomerates)
RF-B	48.6	46	20-100 nm (agglomerates)
Valimet H-2	2.14	1035 ($\sim 1 \mu$)	0.5-3.5 μ spherical
N-35	15.73	141	50-250 irregular shapes
N-40	6.87	322	50-100 irregular shapes
N-41	79.0	28	30-110 spherical
IH	51.3	43	43-64 spherical

Assumptions used to estimate particle diameter from BET surface area:

- Particles have insignificant porosity.
- Particles are composed of perfect spheres of one uniform size.
- Particles are smooth, they have zero level of roughness.
- Density of Al powders is = 2.71 g/cc.

Average particle diameter, d (in nm) was calculated from the BET surface area, A_s (m^2/g) using the following equation:

$$d \text{ (in nm)} = 6000 / (2.71 * A_s)$$

Different methods for determining particle size of UFAl powders

METHOD

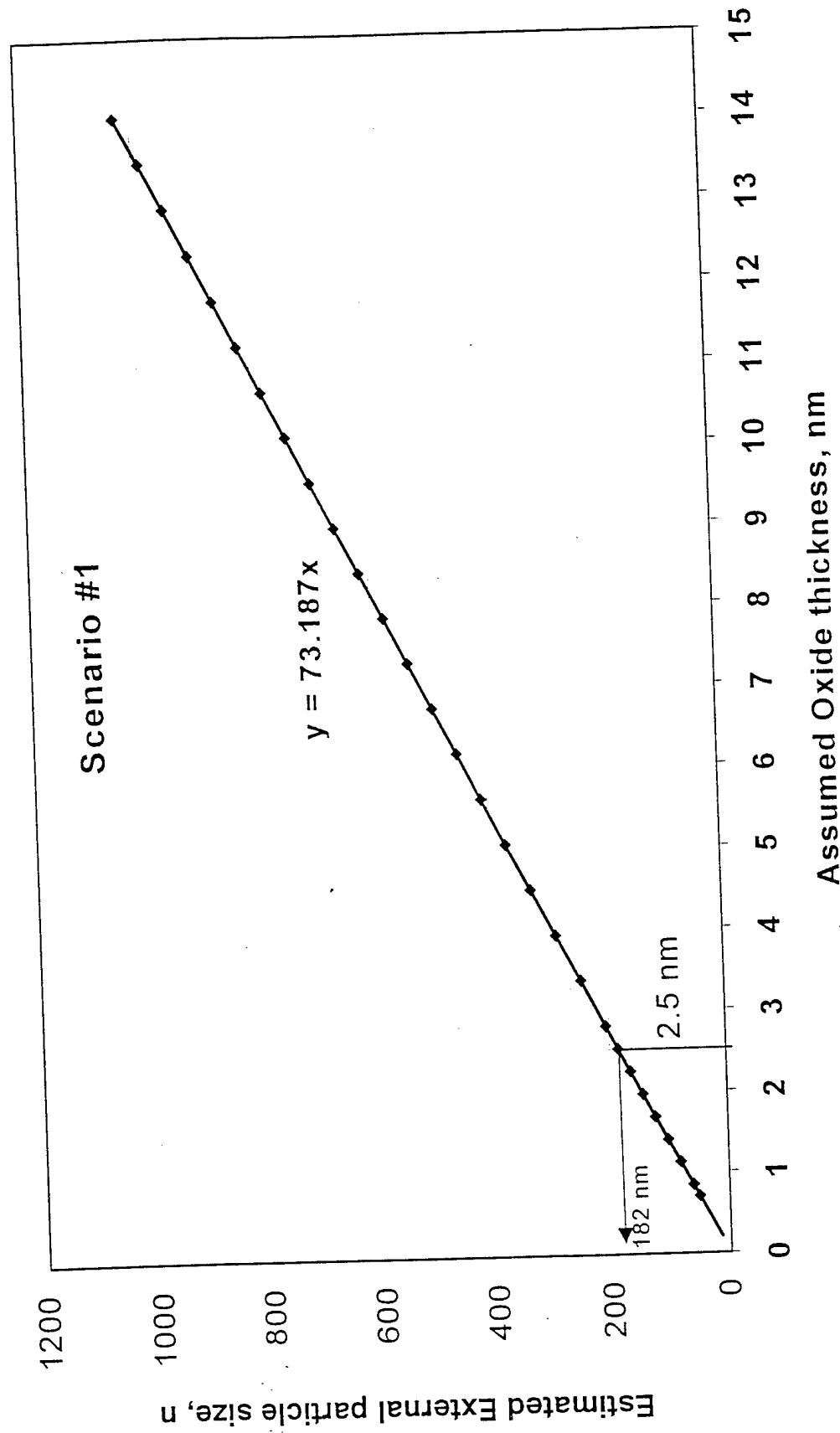
Pros and cons

- | | |
|--|---|
| • Direct from STM and SEM | • Electrostatic causes agglomeration |
| • BET surface area | • All particles assumed spherical <ul style="list-style-type: none">• Gives One average size• No roughness |
| • Direct from TEM cross-sections | • Work in progress |
| • From TGA measurements
see next Three slides | • Need to know thickness of pre-existing Al_2O_3 layer |

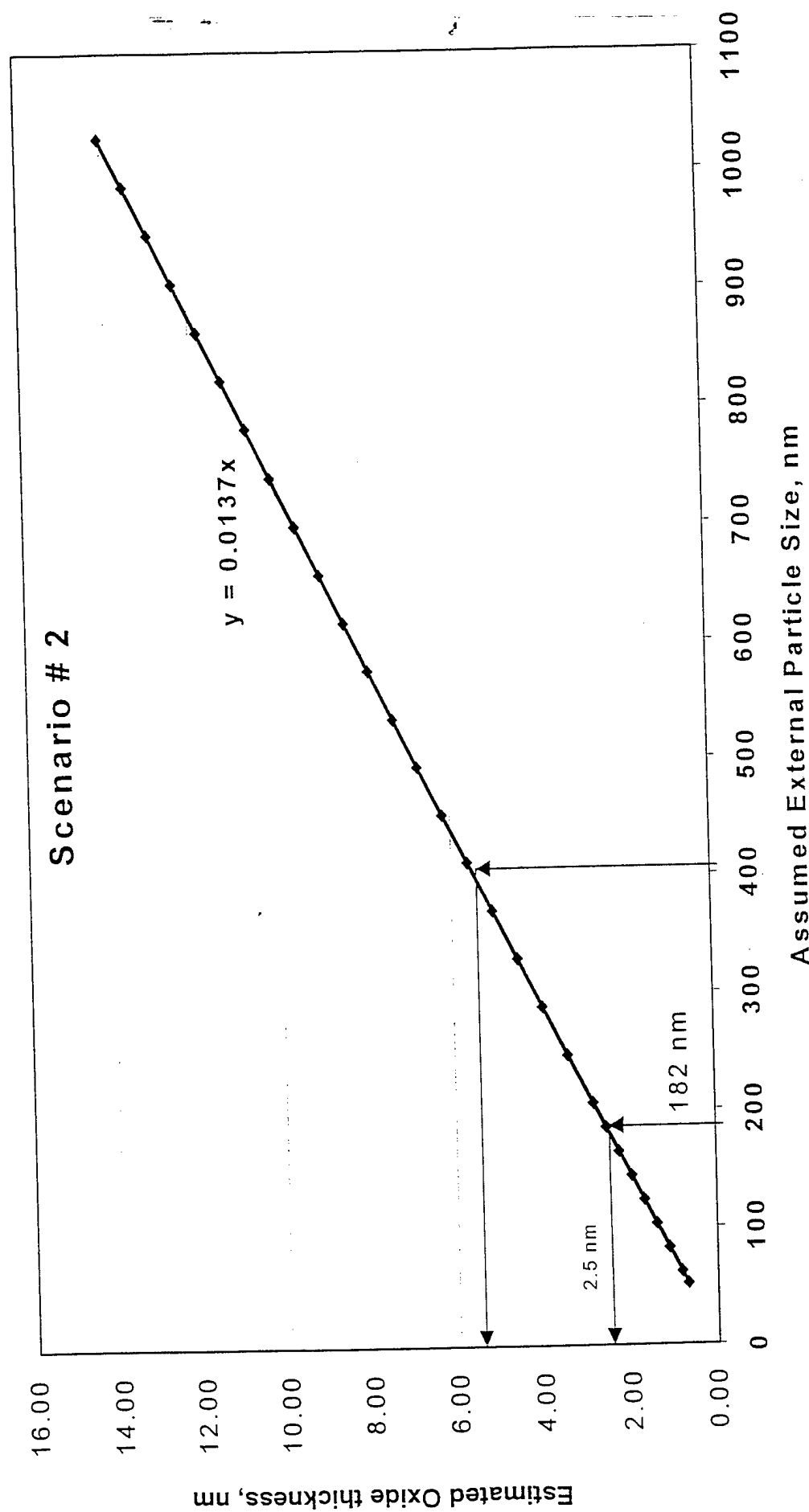
Dependence of percent active aluminum on UFAI starting particle size
(nitridation reaction at 600 C)

<u>Sample</u>	<u>BET size, nm</u>	<u>% Al</u>	<u>% Al₂O₃</u>	<u>Estimated thickness, nm</u>
N-11	40	87.82	12.18	0.61
N-96	41	87.91	12.09	0.62
ALEX	165	89.21	10.79	2.22
N-41	28	85.67	14.33	0.51
RF-A	46	85.47	14.53	0.85
RF-B	46	94.83	5.17	0.29
IH				
IH-small	43	79.63	20.37	1.24
IH-medium	43	82.05	17.95	1.07
IH-large	43	81.13	18.87	1.14
	Average:	80.94	19.06	1.15
Valimet H-2	1035	92.19	7.81	9.92
ALEX-RUSSIAN	183	89.16	10.84	2.48

1. Find percentage of active aluminum (taken here as 90%) after complete nitridation.
2. Assume the balance (10%) as the pre-existing Al_2O_3 layer.
3. Obtain a plot between thickness of oxide layer and particle size.
4. Assume a value for the thickness (e.g., 2.5 nm) and obtain particle size.



1. Find percentage of active aluminum (taken here as 90%) after complete nitridation.
2. Assume the balance (10%) as the pre-existing Al_2O_3 layer.
3. Obtain a plot between particle size and thickness of oxide.
4. Take the particle size of powder as computed by the BET previous calculation.
5. Obtain the corresponding oxide thickness from the plot.



CONCLUSIONS

- Reaction between UFAl powders and nitrogen indicated that the nitridation reaction was completed at 600 C on all samples examined.
- The nitridation reaction forms hexagonal AlN as shown by x-ray diffraction.
- Diffusion of gaseous N₂ from the outer surface of particles through the AlN layer to the inner core of aluminum is not restricted at 600 C.
- Unlike nitridation, the reaction between UFAl powders and O₂ is not always completed at 600 C.
- The completion of oxidation reaction depends on UFAl particle size. For smaller particles (~ 50 nm), the oxidation can be completed at 600 C. For larger particles (~ 1000 nm), the oxidation can ONLY be completed at higher temperatures; as high as 1050 C.
- Diffusion of O₂ through the oxide layer to inner core of aluminum is restricted. The oxide layer is imposing diffusion limitations on oxidation.

RECOMMENDATIONS

- New techniques and methodologies are required to evaluate UFAl.
- Develop a technique for thin coating of UFAl immediately after the particles are born. This treatment will increase the active aluminum content of the sample.
- In order to evaluate the different methods of preparing UFAl powders, samples with different particle sizes ought to be prepared by each method.
- The effect of aging (for example, the exposure of UFAl powders to dry and wet air) needs to be addressed.
- Compatibility between UFAl powders and other propellants, fuels and oxidizers needs to be considered.

ACKNOWLEDGEMENT

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- High Energy Density Matter Program, AFRL Propulsion
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- Ms. Marietta Fernandez for SEM and STM work.